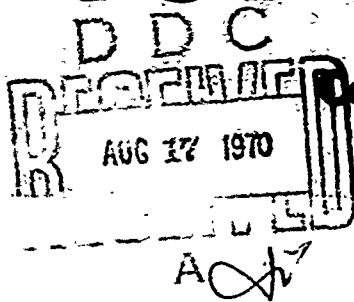


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review

OF RECENT
DEVELOPMENTS

Corrosion and Compatibility

W. E. Barry • August 7, 1970

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ALUMINUM ALLOYS

The cavitation erosion of aluminum in formamide, ethanol, acetone, and glycerol, and mixtures with distilled water has been studied at the California Institute of Technology.⁽¹⁾ Exposure conditions were ± 0.001 inch amplitude, 14 kHz frequency, and 27 C (81 F) temperature. The cavitation damage rates were less in the organics than in water. All except glycerol showed a monotonic decrease in damage going from pure water to pure organic. The water-glycerol solutions exhibited a minimum damage rate in an equimolar solution. Ethanol-glycerol solutions produced a maximum in damage rate at a mole ratio of 2 to 1 of glycerol to ethanol.

A quality-control test has been developed by Alcoa for determining the susceptibility of tempered 7178 and 7075 to exfoliation corrosion and stress-corrosion cracking in the short transverse directions.⁽²⁾ The quality-control test was checked against corrosion tests performed in acidified salt spray and 3.5 percent NaCl solution (alternate immersion). The test consisted of measuring the potential of the aluminum alloy after 35 minutes in 70/30 volume percent $\text{CH}_3\text{OH}/\text{CCl}_4$ containing 5.5 g/l anhydrous CuCl_2 . A difference in potential of several hundred millivolts was developed between the resistant and susceptible conditions (susceptible was more positive). This potential behavior was attributed to the retention of copper on the surface of specimens undergoing intergranular corrosion and to the absence of copper on the surface of specimens undergoing pitting. The copper-covered surfaces assumed the more positive potentials characteristic of copper.

The mechanical, fracture, fatigue, and stress-corrosion properties of a Boeing-recommended aluminum alloy (Alloy 21) have been evaluated by Boeing.⁽³⁾ The alloy contains 6.4 zinc, 2.5 magnesium, 1.1 copper, 0.13 iron, 0.10 manganese, and 0.13 zirconium. A T6 + 35 hour at 325 F heat treatment achieved a 25-ksi short-transverse stress-corrosion threshold for smooth specimens. The mechanical properties of the Alloy 21 were comparable to those of 7049-T73. The fracture toughness was as good, or better than, that of other high-strength aluminum alloys. The smooth and notched-axial (tension-tension) fatigue properties were comparable to those of 7075-T6 and 7075-T73.

A final report on the development of a high-strength aluminum alloy with improved resistance to

stress-corrosion cracking in the short transverse direction has been issued by Alcoa.⁽⁴⁾ The alloys studied included a 7175 control and variations of 5.8 to 7.4 percent zinc, 2.0 to 2.5 percent magnesium, and 2.1 to 2.7 percent copper, with either separate or combined additions of zirconium, manganese, and chromium. All the alloys developed more attractive combinations of strength and hardenability than the 7175 control and exhibited equivalent or better resistance to stress-corrosion cracking. The alloys with the optimum combination of properties contained

Element	Percent
Zinc	5.75 to 6.25
Magnesium	2.0 to 2.5
Copper	2.1 to 2.6
Zirconium	0.09 to 0.15
Silicon	0.10 max
Iron	0.12 max

The effect of microstructure on the stress-corrosion-cracking susceptibility of a high-purity Al-6.8Zn-2.3Mg alloy in 3.5 weight percent NaCl solution has been studied at Carnegie-Mellon University.⁽⁵⁾ Results indicated that the type and size of the matrix precipitate controls susceptibility. The width of the precipitate-free zone adjacent to grain boundaries did not appear to affect susceptibility. The effect of grain-boundary precipitates was not clear, although it appeared that susceptibility could be influenced by the size and spacing of these precipitates under certain conditions. The degree of susceptibility of a microstructure was found to depend on the deformation process which occurs in the microstructure, i.e., the more heterogeneous the deformation, the more susceptible the microstructure. The degree of heterogeneity of the deformation process appeared to depend on whether matrix precipitates can be deformed or whether cross or duplex slip can occur.

BERYLLIUM ALLOYS

The compatibility of beryllium with fluorocarbon solvents has been studied at DuPont.⁽⁶⁾ Unalloyed beryllium samples were exposed 100 hours at 130 F to the following: Freon TF, Freon TMC, Freon T-P35, and Freon T-P35 inhibited. The beryllium was found to be compatible with these solvents. Corrosion rates calculated from weight-change data were 0.02 mil/year in all solvents, and breakdown of the solvents was negligible.

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IRON-BASE ALLOYS

Steels

The effect of impurity additions of sulfur, phosphorus, carbon, chromium, and silicon + manganese on the fracture toughness and stress-corrosion cracking (SCC) of 18Ni (300 grade) maraging steels have been studied at Carnegie-Mellon University.⁽⁷⁾ Stress-corrosion behavior was determined by testing plane-strain fatigue-precracked specimens in 3.5 weight percent NaCl solution. The following results were obtained:

Variable	Fracture Toughness	Resistance to SCC
High-purity heat (0.005C)	Increase	None
0.01 to 0.06 carbon	Decrease	Slight increase
Up to 0.03 phosphorus additions	None	Slight increase
0.24 chromium addition	None	Decrease
Up to 0.03 sulfur additions	None	None
Silicon + manganese additions	Decrease	None

A practical conclusion was drawn from the results that for optimum stress-corrosion resistance and fracture toughness, the 18Ni maraging steel should be as low as possible in both carbon and chromium; the level of the other elements is of much less importance.

Recently evolved Ratio Analysis Diagrams (RAD) for characterization of resistance to fast fracture and for interpretation to failure-safe design were extended by the Naval Research Laboratory to cover the case for stress-corrosion cracking in high-strength steels.⁽⁸⁾ The extension provided dual engineering definitions of flaw size-stress level requirements for failure by fast fracture and stress-corrosion cracking.

Stainless Steels

The resistance of 18-18-2 stainless steel to stress-corrosion crack initiation and propagation in boiling 42 percent MgCl₂ has been studied at U.S. Steel.⁽⁹⁾ The 18-18-2 was hot-roll bonded to a second 18-18-2 alloy modified with molybdenum and phosphorus additions which made it susceptible to stress-corrosion cracking. The resulting sheet was tested in the following conditions: cold worked, annealed at 2000 F and annealed plus sensitized at 1250 F. Half of each set of specimens were stressed into U-bends with the 18-18-2 on the tension side and half with the susceptible alloy on the tension side. No cracking failures occurred with the 18-18-2 on the tension side after 5 months' exposure (3750 hours) to the boiling 42 percent MgCl₂. Cracks initiated in 70 to 284 hours where the susceptible alloy was on the tension side. These cracks propagated transgranularly to the interface and were blunted when they reached the 18-18-2 stainless.

The DuPont Savannah River Laboratory has conducted critical experiments to verify its hypothesis that chloride in alumina corrosion product was

the cause of stress-corrosion cracking of sensitized stainless steel in the Savannah River Reactors.⁽¹⁰⁾ Alumina growing on aluminum was found to absorb chloride from water containing 1 to 2 ppm chloride ion at 100 C. Iron impurity in the alloy enhanced chloride absorption. In the range pH 4 to 7, chloride release was greatest at pH 4 and least at pH 5. Chloride was concluded to be absorbed as the alumina is formed on the hot aluminum cladding on the fuel; the alumina spalls and is transported to the stainless steel surfaces; chloride is released from the alumina by the acidic reaction at anodic sites on the steel; the negative chloride ion is attracted to the positive anodic site and initiates stress-corrosion cracking. Suggested remedies for minimizing cracking were: (1) maintain the coolant at pH 5 to minimize chloride release, (2) eliminate the use of chlorinated solvents as degreasing agents for aluminum, (3) add inhibitors to the coolant, (4) install sacrificial anodes, or (5) remove chloride-bearing alumina from the system.

NICKEL- AND COBALT-BASE ALLOYS

The effect of environment on the high-temperature erosion-corrosion of superalloys is described in a paper from NASA Lewis Research Center.⁽¹¹⁾ The effect of test methods on corrosion behavior and relative rating ranging from simple laboratory tests to complicated rigs simulating engine conditions is discussed. Also presented are examples of specific effects of such variables as thermal cycling, gas velocity, and gas composition on corrosion resistance. Thermal cycling, particularly the frequency of cycling, has a strong influence on corrosion resistance. The effect of high gas velocity was described as a combination of erosion and accelerated vaporization of protective scales.

TITANIUM ALLOYS

Long-term stress-corrosion tests have been conducted by the Marshall Space Flight Center on Ti-6Al-4V alloy in fluids associated with processing and pressure vessels in the Saturn V vehicle.⁽¹²⁾ U-bend samples in triplicate were immersed in each of the fluids for 2 years. Those exposed to absolute methanol failed in 3 to 5 days. The specimens in the following solutions survived 2 years' exposure with no evidence of cracking: RP-1 fuel, acetone, Freon PCA (113), trichloroethylene, isopropyl alcohol, ethyl alcohol, distilled water, monomethyl hydrazine (MMH), hydraulic oil, MIL-H-5606, methylene chloride, methyl ethyl ketone, Aerozine 50, methanol (2 days' pre-exposure) plus MMH, and methanol (2 days' pre-exposure) plus Aerozine 50. In addition, welded specimens were stressed to 115 ksi (snap-in bent beams) and exposed for 2 years to trichloromonofluoromethane and trichlorotrifluoroethane with no evidence of cracking.

The stress-corrosion behavior of Ti-6Al-4V alloy in methanol-water-sodium chloride solutions is being studied at The Ohio State University.⁽¹³⁾ In methanol-0.3 weight percent H₂O-saturated NaCl and at stresses of 80 percent of yield strength, stress-corrosion cracking occurred over the potential range -650 mV to +500 mV (SHE). Applied potential had virtually no effect on crack velocity (about 0.003 mm/sec) once crack initiation had started. Increasing the applied stress decreased the initiation and failure times and increased the crack-propagation rate. Varying the water content produced a minima in the initiation and time-to-failure curves at about

0.2 weight percent water but had no effect on crack-
ing velocity (about 0.003 mm/sec). Increasing the
NaCl content from 0.05 N to 0.20 N in the methanol-
0.3 weight percent H₂O solution caused a progressive
decrease in crack initiation and failure time but
had no effect on crack velocity (about 0.003 mm/sec).

The effect of microstructure on the stress-
corrosion cracking (SCC) susceptibility of Ti-7Al
and Ti-8Al alloys has been studied at the Naval Ship
Research and Development Laboratory.⁽¹⁴⁾ Tests were
conducted in seawater with notched cantilever-beam
specimens. The stress-corrosion fracture path was
transgranular with cracking primarily by cleavage.
The SCC susceptibility was found to be dependent
on the α_2 (Ti₃Al) precipitation reaction. The aging
of alpha-annealed Ti-7Al alloys for times up to 120
hours at 1200 F caused increased susceptibility to
SCC. Aging for 500 hours produced a significant re-
covery of SCC resistance indicating the dependency
of SCC on the coherency of α_2 precipitates. The
susceptibility was increased by large grain size
and α_2 precipitation in Widmanstätten platelet
boundaries.

The effect of pH on the stress-corrosion
cracking of Ti-7Al-2Cu-1Ta alloy in seawater has
been studied by the Naval Ship Engineering Center
and The International Nickel Company.⁽¹⁵⁾ Stressed,
notched specimens were exposed to seawater adjusted
to pH 1 to 11.6 with appropriate additions of HCl or
NaOH. Cracking was transgranular at all pH levels
studied. Cracking susceptibility decreased as the
pH was increased from 1 to 7.4 and appeared to re-
main constant over the range pH 7.4 to 11.6. At
low pH, cracks were at 45 degrees to the surface,
followed the orientation of alpha platelets, and
had a more ductile appearance.

The hot-salt stress-corrosion-cracking be-
havior of titanium alloys is described in a paper
from Lewis Research Center.⁽¹⁶⁾ Attempts were made
to determine why there have been no service failures
from this failure mechanism. A survey of engine
manufacturers revealed that many titanium components
in jet engines operate at temperatures and stress
conditions that cause failures in laboratory stud-
ies. Field surveys at engine-overhaul depots meas-
ured salt deposits accumulated during flight that
were in excess of the minimum amounts that caused
failures in laboratory tests. Studies in a dynamic
air facility simulating environmental conditions in
a compressor revealed that high-velocity air flow
did not eliminate hot-salt cracking. Surface prep-
aration that produced compressive surface stresses
was found to cause a marked reduction in susceptibil-
ity to hot-salt stress corrosion.

MISCELLANEOUS

Chemical rocket/propellant hazards handbooks
have been issued by the Hazards Working Group JANAF
Propulsion Committee.^(17,18) The publications are
a source of information and a set of basic guide-
lines for the processing, handling, storage, and
transportation of these materials. The handbook
on chemical, solid, rocket propellants and propel-
lant ingredients contains chapters on Hazard Analy-
sis; Propellant Manufacture; Packaging; Storage
Surveillance, and Transportation; Assembly, Launch
and Static Test; Facilities; and Waste Disposal.
The handbook on liquid propellants and oxidizers
contains 21 chapters on the safety and hazards as-
pects of some 30 materials. Chemical and physical

data are presented together with those on environ-
mental health, toxicity, fire, and explosion hazards.
Also included are recommended methods for equipment
cleaning, firefighting, disposal, and means for pro-
viding personnel protection.

The rain erosion of aluminum 1145, polymethyl-
methacrylate plastic and coated materials has been
studied by Textron-Bell Aerosystems Company.⁽¹⁹⁾
Drop sizes were 1.8 to 2.0 mm and velocities were
730 to 1120 ft/sec. In the aluminum, the weight loss
due to erosion increased with time, though not mono-
tonically. In the early stages of erosion, the pri-
mary mechanism of weight loss was the shear off of
the lips of small, dimpled pits. In later stages,
the pits deepened and aggregated, isolating small
islands of metal which were then lost. The erosion
of polymethylmethacrylate was similar, but the ini-
tiation and acceleration of erosion were the result
of the formation and propagation of brittle cracks.
The erosion of coated-composite materials depended
on several factors including the hardness of the coat-
ing. With soft coatings, such as urethane, erosion
began with fracture of the composite beneath the
coating, while with hard coatings, such as metal or
ceramic, the erosion began in the coating material.

The rain-erosion resistance of protective coat-
ings on aluminum has also been studied in England.⁽²⁰⁾
Tests were conducted under standard conditions of
1 in./hr rain at 500 miles/hr with an impact angle of
90 degrees. The coatings studied included polyure-
thane, neoprene, sprayed alumina, and nitrile rubber.
Polyurethane coatings were the most protective. To
achieve maximum performance from coatings, it was es-
sential to apply them at least 0.010 in. thick and to
obtain a good adhesive bond with the substrate. The
use of fillers to remove surface defects prior to
applying the coating to laminates was not satisfac-
tory. A better method was to apply a gel coat of the
same resin as used in the manufacture of the laminate.

At the National Bureau of Standards, corro-
sion rates obtained by polarization techniques have
been compared with rates obtained from weight-change
data using the same specimens.⁽²¹⁾ The following ma-
terials were exposed 9 months to synthetic seawater
at room temperature: ingot iron, ingot Fe-26.5Ni
plus 2 to 20 Cr, Type 304 stainless steel, Ni-resist
Type 1, Ti-4Al-4Mn, 90Cu-10Ni, 70Cu-30Ni, Naval brass,
aluminum brass, Admiralty brass, Olin alloy 194 (97Cu-
2.3Fe), Monel 400, Incoloy 825, and 5454 aluminum.
Corrosion rates calculated from breaks in the polari-
zation curve (Pearson method) or from polarization
resistance (Stern-Geary method) agreed reasonably well
with the actual weight losses. Also demonstrated was
that polarization techniques can be used to evaluate
galvanic effects on the anodic member of a galvanic
couple.

The corrosion of Inconel 600 and Zircaloy-2 in
pH 10 (LiOH) water at 288 C (550 F) has been studied
with linear-polarization techniques at Knolls Atomic
Power Laboratory.⁽²²⁾ Corrosion rates calculated from
the linear-polarization data were correlated with
posttest weight-change measurements. With 35 cc
hydrogen/kg dissolved in the water, the electrochemi-
cally determined rates for Inconel 600 were much
higher than those obtained from weight change. Good
agreement was obtained in the results obtained for
Zircaloy-2 under the same conditions. With dissolved
hydrogen in the water, the Inconel 600 was concluded
to have a much higher exchange current for hydrogen
than a corrosion current and thus an accurate

corrosion rate could not be determined by the linear-polarization method.

The solid-electrolyte technique has been used to study the oxidation of iron and molybdenum at Lewis Research Center.⁽²³⁾ Accurate kinetic and thermodynamic data were obtained by this method. The technique consisted of pressing a thin metal foil (iron) onto an electrolyte disk ($ZrO_2 + CaO$). A mixture of CO and CO_2 was directed against the metal foil, and air or oxygen was directed against the opposite side of the electrolyte disk. Prior to heating to temperature, sufficient voltage was imposed on the cell to prevent oxidation and the CO/CO_2 ratio was made slightly reducing. After thermal equilibrium was obtained, the gas ratio was suddenly changed to the desired level. Initially, the potential dropped as oxygen was absorbed on the surface. The potential then remained relatively constant as the foil was converted to the oxide (wüstite), after which the potential dropped to a lower level depending on the oxygen differential. From these data a linear reaction rate was calculated.

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